Chemical & Engineering NEWS

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Peer Review

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Electrolytic cell membrane development surges

Perfluorinated membranes offer chlor-alkali producers energy savings and less pollution; firms vie for share of growing market

Stephen C. Stinson
C&EN, New York

Energy savings and pollution control needs of the chlor-alkali industry have teamed up with accelerated competition among electrolytic cell membrane producers to spark development of new, more efficient membranes. Competitive intensity also has led membrane producers to disclose more of their technology than ever before, in efforts to persuade prospective customers of their expertise.

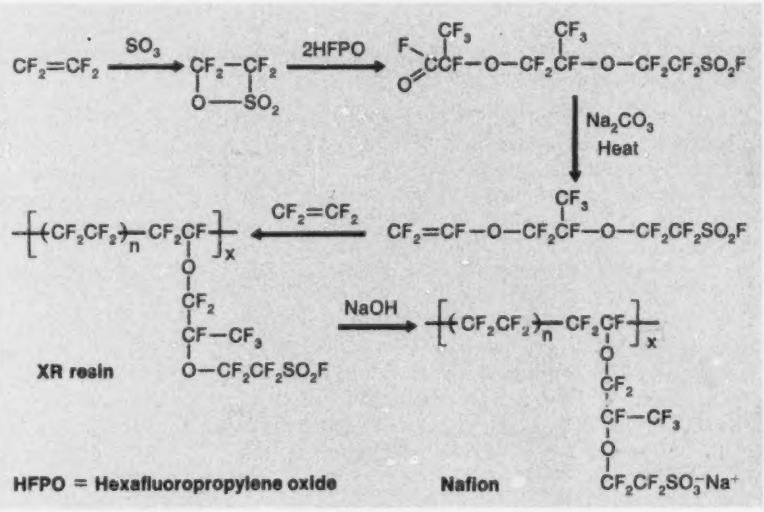
Increased membrane production capacity to meet the needs of the chlor-alkali industry may mean increased supplies of membranes at competitive prices for development of such other applications as hydrogen production, fuel cells, energy storage systems, pollution control devices, and catalysts. Some of these other applications may result from work of academic chemists, attracted by the unique ion and fluid transport properties of these membranes.

The membranes are perfluorinated ionomer membranes containing sulfonate and/or carboxylate groups in the resin. These anionic groups almost completely inhibit transport of hydroxide ions from the cathode compartment of a chlor-alkali cell, while letting current flow in the form of sodium ions. The result is production of caustic that is purer and more concentated than that from diaphragm cells. And the membrane cells avoid potential pollution from mercury cells (C&EN, March 20, 1978, page 20).

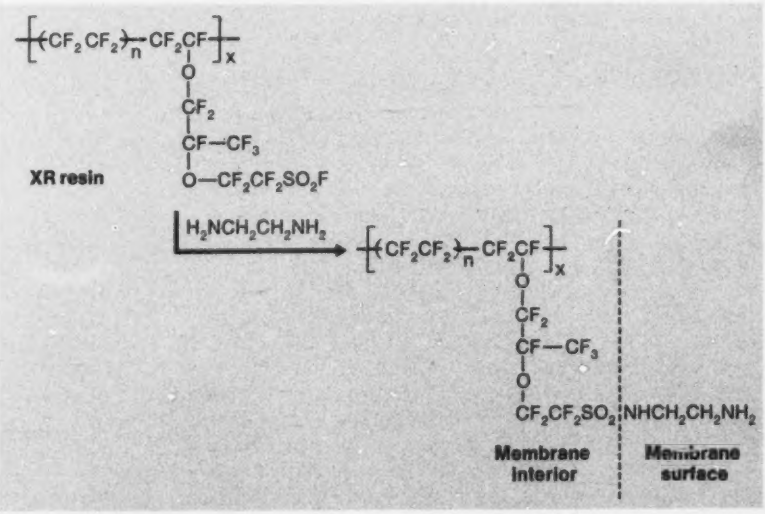
New developments in perfluorinated membranes, coupled with companies' increased willingness to talk about their materials, led the American Chemical Society's Division of Polymer Chemistry to organize a workshop on the subject that was held recently in Lake Buena Vista, Fla.

The four companies now jockeying for position in the worldwide chlor-alkali cell membrane market are Asahi Chemical Industry, Tokyo; Asahi Glass Co., Yokohama; Du Pont, Wilmington, Del.; and Tokuyama Soda Co., Tokyo. The stakes are high. Paul Henstridge, membrane cell business manager at Imperial Chemical Industries, a chlor-alkali cell maker, estimates that chlor-alkali producers in noncommunist countries will add 22 billion lb per year of new chlorine capacity by 1990. If all of this capacity were membrane cells, which now seem the favored route, these plants would need 3.3 million to 4.4 million sq ft of membrane, worth $13 million to $18 million at current prices. Also, because membranes may last only one to two years, membrane produc-

Du Pont Nafion membranes were the first of their kind...



...which sometimes got a surface treatment



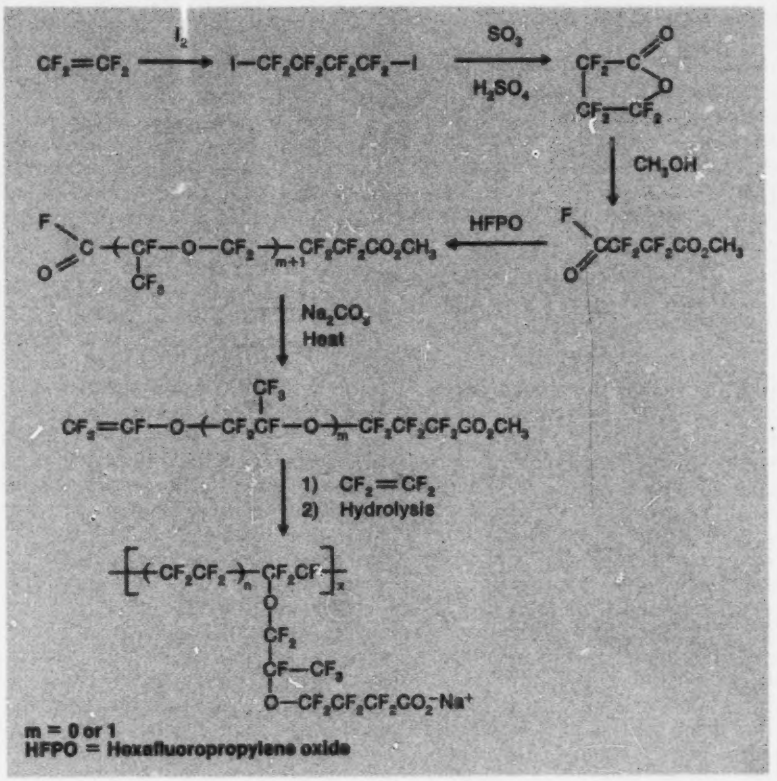
ers would see a lot of repeat orders. Ultimately, with conversion of all chlor-alkali production to membrane cells in noncommunist countries, the annual market may be $250 million.

Roger A. Smith of Du Pont described the company's newest entry for the chlor-alkali market, Nafion 901. The new membrane has a perfluorocarboxylate resin layer perhaps 70 μm thick, laminated to a perfluorosulfonate membrane 100 to 300 μm thick, with the whole assembly probably reinforced by a woven polytetrafluoroethylene backing. This two-layer membrane, with the carboxylate layer facing the cathode (caustic) compartment, is intended to retain the high conductivity of perfluorosulfonate while improving current efficiency by impeding back migration of hydroxide into the anode compartment. The perfluorinated resins make the membranes resistant to high cell operating temperatures and the degrading effects of chlorine and caustic.

Du Pont developed the first perfluorinated ionomer membranes about 20 years ago during work with GE on a fuel cell. The company copolymerizes tetrafluoroethylene with a perfluorovinyl ether sulfonyl fluoride. Production of the sulfonate monomer begins with reaction of tetrafluoroethylene with sulfur trioxide to form 2-hydroxyethanesulfonic acid sultone. The sultone rearranges to fluorocarbonylmethanesulfonyl fluoride, which Du Pont reacts with 2 moles of hexafluoropropylene oxide to yield a compound with a terminal 1-fluorocarbonyltrifluoroethoxy group. This group loses carbonyl fluoride on heating with such catalysts as sodium carbonate to give the vinyl monomer. Du Pont converts the sulfonyl fluoride form of the copolymer resin to a more thermoplastic sulfonyl chloride for processing, then hydrolyzes with potassium hydroxide solution to the sulfonate form.

Though sodium and water transport and conductivity are high for plain sulfonate membranes, back migration of hydroxide is excessive. Working on the idea that high membrane water content lowered the barrier to hydroxide ions, Du Pont scientists developed membranes with a higher equivalent weight layer facing the cathode compartment, then added a surface treatment with ethylenediamine. Reaction of the cathode-side surface in the sulfonyl fluoride form with ethylenediamine produced N-β-aminoethylsulfonamide groups facing that side. These groups

Asahi Glass developed monomers for carboxylate resins



were more weakly acidic than sulfonic acid groups and thus retained less water. But the lifetimes of surface-treated membranes were too short in chlor-alkali cells.

Du Pont has signed an agreement with Asahi Glass to cross-license patents, and it may be that Du Pont's carboxylate layer is made according to Asahi Glass technology. Maomi Seko of Asahi Chemical has criticized the approach involving formation of a carboxylate layer by lamination, saying that adding the layer decreases electrical conductivity excessively. Du Pont scientists may have opted to make the membrane more robust and longer-lived by lamination, thus saving frequent replacement costs to users.

Asahi Chemical's Seko, in describing the firm's membrane chemistry, says that in addition to favoring a surface carboxylation treatment for sulfonate ionomer membranes, Asahi Chemical scientists also worked to develop a lower-molecular-weight comonomer for tetrafluoroethylene to lower equivalent weights of copolymer resins. His company devised syntheses of a series of terminal perfluorovinyloxyalkane-sulfonyl fluorides and terminal perfluoro(α-methyl-β-vinyloxy)ethoxyalkanesulfonyl fluorides for this purpose.

Asahi Chemical makes the cathode side of the tetrafluoroethylene copolymer membrane resistant to hydroxide back migration by surface oxidation of sulfonyl to carboxylate groups. Seko says his firm converts sulfonyl fluoride to sulfonyl chloride groups, reduces surface sulfonyl chloride to sulfenic acid groups, then oxididizes sulfenic acid to carboxylate groups. The resulting carboxylate layer of the membrane is 2 to 10 μm thick, he says.

The Tokuyama Soda approach also involves surface oxidation to carboxylate groups, according to senior chief researcher Toshikatsu Sata. The company begins with Du Pont Nafion in the sulfonyl chloride form, coats the surface with an alcohol, and subjects the alcohol-wetted surface to air oxidation. This is also the technique used by Asahi Chemical until 1976, when the company turned from Nafion to membranes made from tetrafluoroethylene and its own comonomers.

Asahi Glass departs from technology of the other three companies in producing an all-carboxylate ionomer membrane. Hiroshi Ukihashi says

Asahi Chemical leads in membrane chlor-alkali capacity

Thousands of metric tons per year	Caustic capacity[a]	Market share %
Asahi Chemical	520	69%
Diamond Shamrock[b]	121	16
Asahi Glass	42	6
Hooker & Uhde[b]	42	6
Tokuyama Soda	14	2
Ionics & Celleco[b]	11	1
TOTAL	750	100%

a Installed or under construction. b Firms using Du Pont Nafion membranes. Source: Asahi Chemical Industry

that his firm has developed perfluorocarboxylate monomers for copolymerization with tetrafluoroethylene. The firm treats tetrafluoroethylene with iodine to give 1,4-diiodooctafluorobutane, which reacts with fuming sulfuric acid to form tetrafluorobutyrolactone. Methanol converts the lactone to tetrafluorosuccinic acid monomethyl ester acid fluoride. Reaction of the acid fluoride with 1 or 2 moles of hexafluoropropylene oxide yields compounds with terminal fluorocarbonyl groups. After heating with sodium carbonate, these monomers are copolymerized with tetrafluoroethylene. Alkaline hydrolysis of the methyl ester groups produces membrane resins. Ukihashi says the methyl ester form of the resin does not decompose at temperatures below 320 °C and is melt-processable into membranes by injection molding or extrusion at melt temperatures of 200 to 250 °C.

One striking feature of industry presentations on all four membrane types was the routine reporting of current efficiencies of 95% or more. Seko of Asahi Chemical reported 96% for its membrane; Ukihashi of Asahi Glass, 97% for its Flemion membranes; Smith of Du Pont, 94.5 to 96.5% for Nafion 901; and Sata of Tokuyama Soda, 93 to 95% for its Neosepta-F membranes. This compared with 50% for unmodified Nafion, Sata said.

These high current efficiencies translate into lower power consumption per unit of caustic produced. For example, Seko of Asahi Chemical reported 2100 kWh per metric ton at 3 kiloamperes (kamp) per square meter and 1950 kWh at 2 kamp per sq m, while Smith of Du Pont reported 2400 to 2600 kWh at 3 kamp per sq m and 2200 kWh at 2 kamp per sq m. These figures compare with 2800 kWh for the mercury cell and 2180 kWh for the diaphragm cell. Thus the new membrane materials have tipped the balance away from diaphragm cells on the basis of power consumption alone, without even considering the low concentrations and high sodium chloride contents of diaphragm cell caustic solution product.

The decreased permeability of the four membrane types to hydroxide ions also has increased the maximum caustic solution concentrations tolerable for high current efficiencies. Three of the four firms have developed membranes for 20% caustic solution and a higher concentration, depending on user needs. The 20% membranes have lower equivalent weights than membrane resins for higher concentrations. Asahi Chemical has membranes for 21% and 30% caustic; Asahi Glass has Flemion membranes for 20% and 35 to 40% caustic, as well as a membrane designed especially for 35% potassium hydroxide; Du Pont's Nafion 901 produces 33% caustic; and Tokuyama Soda's two Neosepta-F membranes are for 20% and 27% caustic. These maximum caustic concentrations compare with 28% achieved by membrane cells of only four years ago.

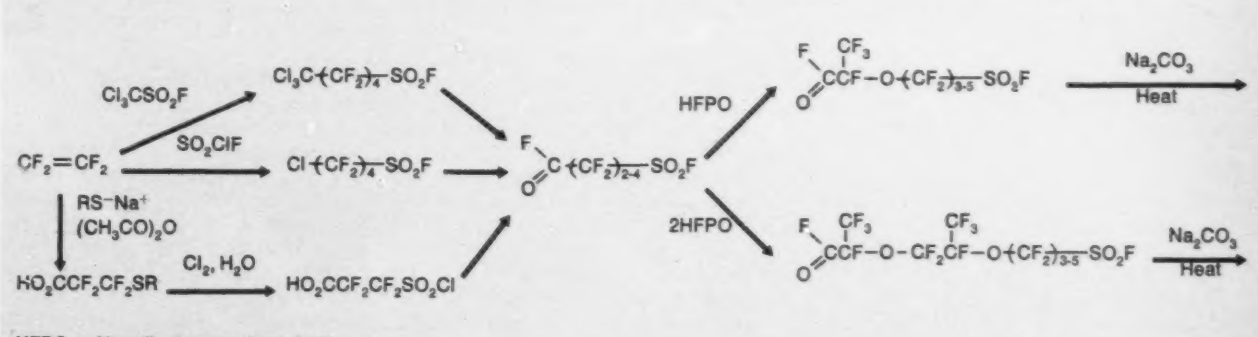
For the future, even further increases in current efficiency as well as reductions in cell volume may come from use of perfluorinated ionomer membranes as solid polymer electrolytes. In such cells, the polymer itself is the only electrolyte. Both surfaces are coated with metal particles to act as current collectors and as anode and cathode. Companies working on solid polymer electrolyte technology include Asahi Glass and Oronzio de Nora Impianti Elettrochimici, Milan, Italy. De Nora has signed an agreement with Dow Chemical, Midland, Mich., to develop such technology (C&EN, June 1, 1981, page 19).

Asahi Glass has reported producing 35% caustic in a solid polymer electrolyte cell at 1950 kWh per metric ton of caustic at 2 kamp per sq m and 2140 kWh at 4 kamp per sq m. De Nora has produced 28 to 30% caustic at 2200 kWh per metric ton and 3.3 kamp per sq m.

As Seko of Asahi Chemical points out, there is now 750,000 metric tons per year of caustic capacity based on membrane cells either installed or under construction worldwide, but none in the U.S. The first such U.S. plant may be the 200 metric-ton-per-day expansion by Vulcan Materials Co., at its Wichita, Kan., plant, scheduled to come on stream in 1983 with Nafion membranes.

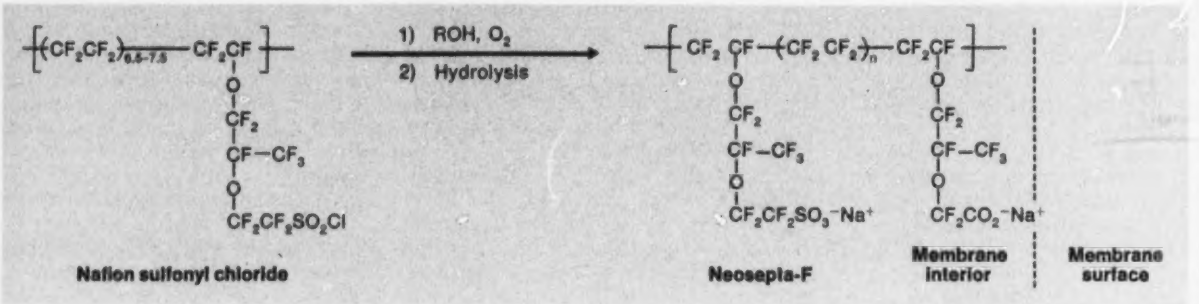
Beyond uses in the chlor-alkali industry, there are specialty applications for perfluorinated ionomer membranes in other electrolytes and in fuel cells. As Anthony B. LaConti of GE, Wilmington, Mass., points out, a GE fuel cell generated electricity from a hydrogen-oxygen reaction in the Gemini space missions;

Asahi Chemical monomers shorten side-chain lengths to lower copolymer equivalent weights



HFPO = Hexafluoropropylene oxide

Tokuyama Soda oxidizes Nafion membrane surfaces



and GE and other firms make water electrolyzers to generate oxygen aboard spacecraft and submarines, as well as hydrogen for chromatographs.

Nevertheless, the feasibility of such large-scale applications as hydrogen fuel or feedstock, combined electrolyzer-fuel cells as load levelers at electric power plants, or batteries for other purposes will be limited by the high cost of membranes. Du Pont's price for Nafion 901 is $460 per sq m. The three Japanese firms won't reveal their prices, but they are probably about the same. To cover high capital investment costs at these prices, water electrolyzers would have to run for long periods at the very high current densities of 10 to 20 kamp per sq m, a feat that seems beyond present membranes. Smith of Du Pont says that Nafion 901 membrane lifetimes might be measured in years as opposed to present one- to two-year lifetimes in the chlor-alkali industry. Membranes for large-scale hydrogen production would have to run at least five years.

Any electrolytic or fuel cell process would have to compete with alternative systems that do not use membranes. Such competition is possible in the chlor-alkali industry, because there is no other way to make chlorine and caustic than by electrolysis, and membrane cells clearly have emerged as superior to other cells. There is no such limited number of candidates for high-capacity batteries, and hydrogen is available at less cost from natural gas.

In a review of perfluorinated ionomer applications, chemistry professor Brian Kipling of the University of Calgary, Alta., noted that these membranes have been used to treat metal plating wastes, to catalyze organic chemical reactions, and to dry gases. Kipling cited work at Du Pont to demonstrate that chromium plating wastes with small amounts of iron, copper, and nickel could be treated to recover chromic acid for reuse. Lead anodes oxidize spent chromium(III) to chromium(VI), while other cations migrate through the membrane into the cathode compartment. The membrane inhibits migration of unwanted anions from the cathode into the anode compartment.

Another method Kipling cites for use in plating wastes is Donnan dialysis. In the Donnan principle, a concentrated solution of, for example, sodium chloride or sulfuric acid is separated by a membrane from a dilute solution of cations. Sodium or hydrogen ions migrate into the solution to be treated, matched by an equal number of equivalents of heavy metal cations that migrate out of the treated water. The resulting concentration of heavy metal cations produces a smaller volume of solution to be treated by other methods like precipitation.

In catalysis research, Kipling notes that organic chemistry professor George A. Olah had used the sulfonic acid form of Nafion at the University of Southern California, Los Angeles, to catalyze Friedel-Crafts reactions at relatively low temperatures.

Chemistry professor William M. Risen Jr. of Brown University, Providence, R.I., uses membranes in his work to catalyze gas-phase reactions. In one experiment, he soaked Nafion membranes in platinum(II) solutions, then warmed the membranes to dry them somewhat. He suggested that water removal may produce vacant coordination sites about platinum, making it coordinately unsaturated and a favorable acceptor for gas molecules. On passing carbon monoxide through the membrane, he observed production of carbon dioxide and hydrogen. In synthesis gas plants, this shift reaction is carried out by other means to produce hydrogen.

For gas drying, Kipling says that Perma Pure Products, Oceanport, N.J., makes units for this use. Moist gas flows in one direction through a Nafion tube, while a dry purge gas flows in the opposite direction in an outer jacket. The removal of water from the moist gas is based on the relatively faster transport of water than other gas molecules through Nafion. □